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The preparation of *meso*-substituted tetrafuryl-porphines is described. These new compounds are very soluble either in organic solvent or in water depending upon the furyl groups substitution. Their spectroscopic absorption, nmr characteristics, and some of their electrochemical properties are reported.

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Synthesis of *meso*-substituted porphyrins and their respective metallo derivative compounds have been investigated for many years in order to study electron-withdrawing or donating groups on spectroscopic data (1), redox potentials (2) or other physico-chemical properties (3). For these purposes *meso*-tetraphenylporphine has been substituted by various functional groups on the *para* or *meta* phenyl position (1,4). In particular the presence of acid or basic groups has provided water soluble porphine derivatives (5). Few compounds have been synthesized in the *ortho*-substituted series because the yield of porphine decreases as the bulk of the substituent increases (4). The *o*-carboxy derivative has never been obtained in this series by the fact that 2-carboxybenzaldehyde derivatives exist as an equilibrium with the 3-hydroxyphthalide form.

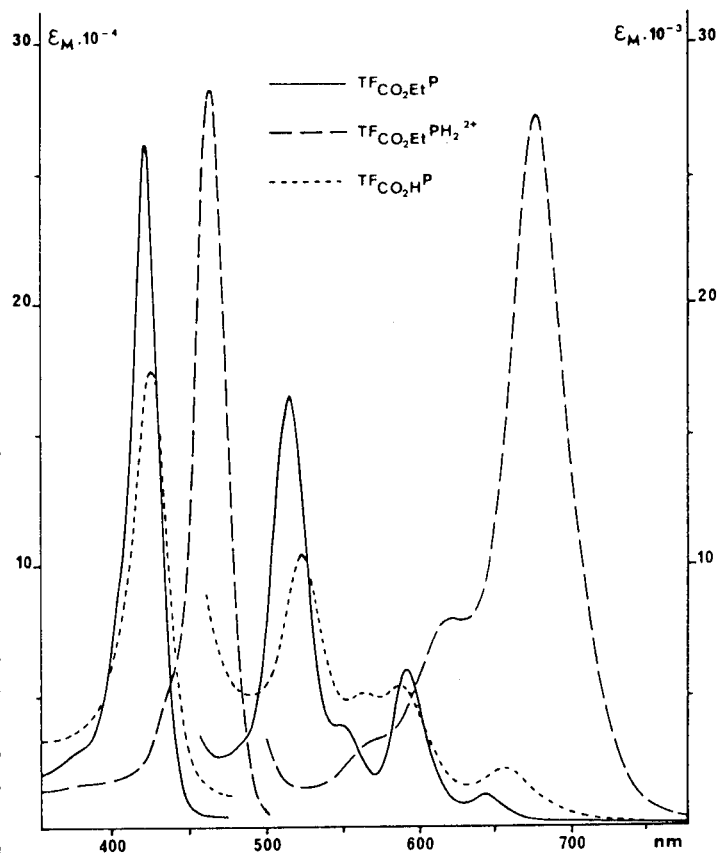
We now report the first synthesis of a new porphine bearing furyl substituted groups in *meso* position. *Meso*-tetra[2-(3-carboxyethyl)furyl]porphine [TF₂CO₂Et^P] (**3a**) was obtained by acid condensation of pyrrole (1) with ethyl (2-formyl)-3-furoate (2) (6) following the method of Treibs and Haberle (7). The porphine did not crystallize by cooling the reaction mixture to room temperature. It was extracted by diethyl ether from the residue obtained after evaporation of the solution to dryness and chromatographed on a silica gel column with chloroform.

When furfural was condensed with pyrrole under the same conditions, no macrocyclic compound was isolated. Thus the use of compound 2, in which the presence of carboxyethyl group stabilizes the heterocyclic ring, appears to be a convenient route for the preparation of this type of porphine.

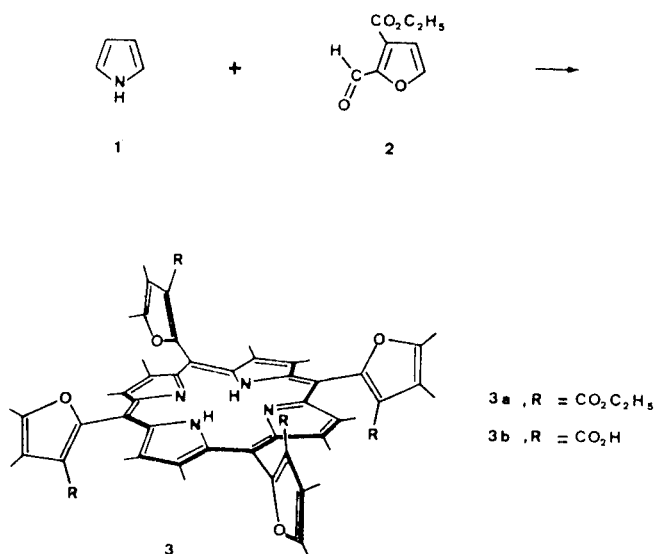
Evidence for the correctness of the structure of the compound was provided by the nmr spectrum (in deuteriochloroform) in which the signals of the pyrrole protons and imino protons of the porphine ring occur at +8.88 and -2.82 ppm, respectively. The other signals were easily assigned to the furyl protons (two doublets at 7.4 and 8.0 ppm) and to the methyl and methylene protons of ethyl ester groups (two multiplets at 0.2 and 3.64 ppm respectively). These last multiplets are consistent with a

four atropisomers mixture, similar to those obtained with *ortho*-substituted *meso*-tetraphenylporphine (8).

The spectral properties of **3a** reflect its aromatic character and overall resemblance to that of porphyrins [λ max (chloroform) 422, 515, 547, 591 and 644 nm; ϵ , 265,300, 17,000, 3,900, 6,050 and 1,460 $M^{-1} cm^{-1}$, respectively]. However, some noticeable differences are observed. The visible range absorption is very different from those reported for *meso*-tetraphenylporphine which possesses an "etio" type spectrum. The extinction coefficient of band I is very small, but the most important difference is in the absorption of band III, near 550 nm, which is reduced to a shoulder. Such spectral variations are also present in *meso*-tetraphenylporphines with an



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electron-withdrawing substituent in *ortho*-phenyl positions (4). By addition of trifluoroacetic acid, a dicationic form is obtained. Its absorption spectrum is characterized by a Soret band shifted more to the red as compared to that of the *meso*-tetraphenylporphyrine dication [λ_{max} (chloroform) 463 and 677 nm; ϵ , 287,000 and 27,850 $M^{-1} \text{ cm}^{-1}$].

Electrochemical studies have been carried out on **3** in dimethylformamide with dried tetrabutylammonium tetrafluoroborate as electrolytic salt. It is reduced in two successive one-electron steps, at - 0.825 and - 1.355 v, on the dropping mercury electrode. These two reduction steps are reversible processes involving the formation of the monoanion and dianion. A third reduction step is observed at - 2.20 v corresponding to an irreversible three electron transfer. The difference between the potentials of the first and second wave, $\Delta = 0.530$ v, is more important than that observed for the other *meso*-substituted porphyrins (2,9). The changes in the electrochemical reactivity induced by the electron-withdrawing furyl *meso*-substituents are indicative of the decreasing porphyrin ring basicity.

When **3** was saponified with potassium hydroxide in a water-ethanol mixture, a 95% yield of *meso*-tetra(3-carboxyfuryl)porphyrin [$\text{TF}(\text{CO}_2\text{H})_4\text{P}$] (**3b**) was isolated after acidification. This compound is soluble in water [λ_{max}

(0.5 *M* borate buffer, pH 8.4) 425, 521, 563, 585 and 656 nm; ϵ , 175,000, 10,400, 5,200, 5,460 and 2,360 $M^{-1} \text{ cm}^{-1}$, respectively].

In the light of these results, it appears that the presence of a heterocyclic furyl group as a *meso*-substituent modifies slightly the spectroscopic and electrochemical behavior of the macrocycle as compared with *meso*-tetraphenylporphyrine. This new *meso*-substituted porphyrin will permit an extensive comparative investigation of the metal derivatives in both organic and aqueous solvents.

EXPERIMENTAL

Mixture of ethyl (2-formyl)-3-furoate (**2**) (39 g.) and pyrrole (**1**) (16.1 ml.) in acetic acid and dry pyridine (800 and 400 ml., respectively) was refluxed for 40 minutes. After cooling, the solvents were removed under reduced pressure. The residue was extracted several times with ether until the extracts were almost colourless. The ether was evaporated. The compound was dissolved in a minimum volume of hot chloroform and crystallized by addition of methanol. After filtration, the solid compound was chromatographed on silica gel (Merck) in chloroform. The porphyrin fraction was evaporated to dryness under reduced pressure and the residue recrystallized from benzene to give the desired porphyrin (1.74 g., 3.48%).

Anal. Calcd. for $\text{C}_{48}\text{H}_{38}\text{N}_4\text{O}_{12} \cdot 1/2(\text{C}_6\text{H}_6)$: C, 67.92; H, 4.55; N, 6.22. Found: C, 67.55; H, 4.53; N, 5.76.

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